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Reptation in artificial tubes and the corset effect of confined polymer dynamics

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Abstract

A spinodal demixing technique was employed for the preparation of linear poly(ethylene oxide) (PEO) confined to nanoscopic strands which in turn are embedded in a quasi-solid and impenetrable methacrylate matrix. Both the molecular weight of the PEO and the mean diameter of the strands are variable to a certain degree. Chain dynamics of the PEO in the molten state was examined with the aid of field-gradient NMR diffusometry (time scale: 10-2 s... 100 s) and field-cycling NMR relaxometry (time scale: 10 -9 s... 10-4 s). The dominating mechanism for translational displacements probed in the nanoscopic strands by either technique is shown to be reptation. A corresponding evaluation formalism for NMR difrusometry is presented. It permits the estimation of the mean PEO strand diameter. Depending on the chemical composition of the matrix, the diameters range from 9 to 58 nm. The strands were visualized by electron microscopy. On the time scale of spin-lattice relaxation time measurements, the frequency dependence signature of reptation, that is T1 ∝ νV 3/4, showed up in all samples. A "tube" diameter of only 0.6 nm was concluded to be effective on this time scale even when the strand diameter was larger than the radius of gyration of the PEO random coils. This "corset effect" is traced back to the lack of the local fluctuation capacity of the free volume in nanoscopic confinements. The confinement dimension is estimated at which the cross-over from "confined" to "bulk" chain dynamics is expected.